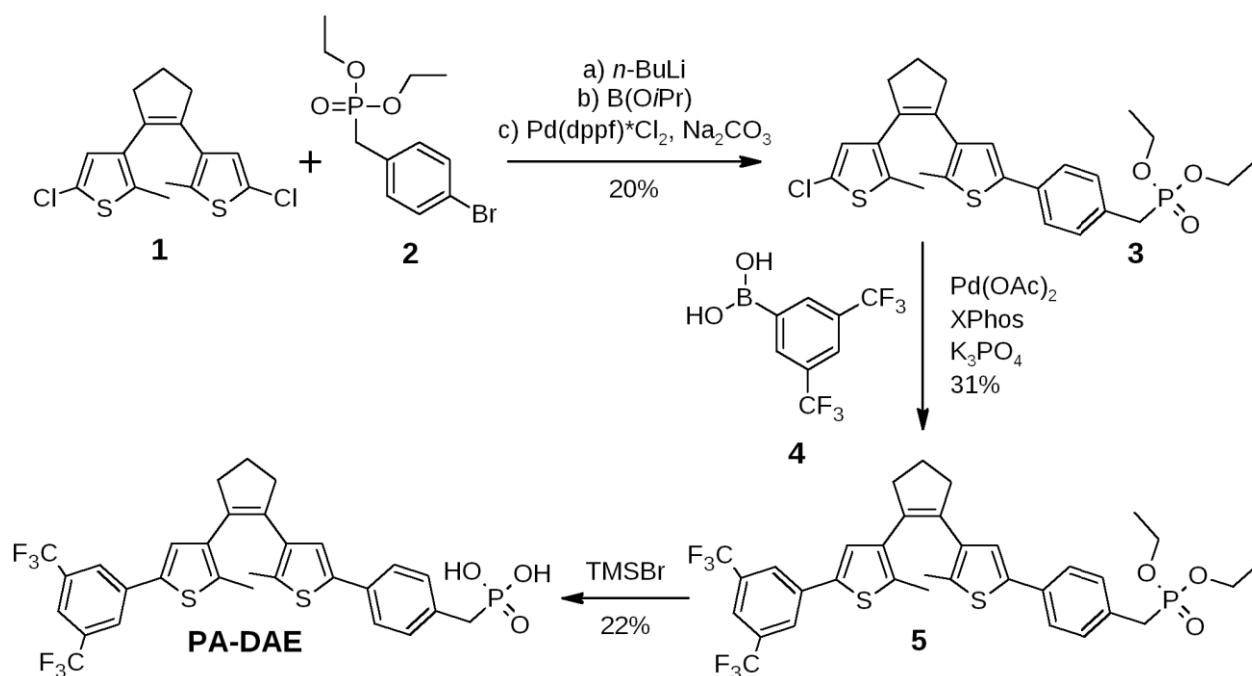


Supporting Information

Dynamic photoswitching of electron energy levels at hybrid ZnO/organic photochromic molecule junctions

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1. Synthesis of PA-DAE switches



Diethyl (4-bromobenzyl)phosphonate (**2**)

In analogy to a literature procedure,^[1] a mixture of 4-bromobenzylbromide (10.0 g, 40 mmol) and triethyl phosphite (7.9 mL, 46 mmol, $\rho = 0.97 \text{ g cm}^{-3}$) was refluxed for 3 h under an argon atmosphere. After cooling to room temperature, the reaction mixture was diluted with water and ethyl acetate. The organic phase was separated, dried (MgSO_4) and all volatiles were removed. Phosphonic ester **2** was obtained in quantitative yield and used without further purification.

¹H-NMR (300 MHz, CDCl₃) δ [ppm] = 7.46 – 7.39 (m, 2H), 7.21 – 7.13 (m, 2H), 4.02 (dq, J = 8.3, 7.1, 1.2 Hz, 4H), 3.09 (d, J = 21.7 Hz, 2H), 1.25 (dt, J = 7.1, 3.5 Hz, 6H).

¹³C-NMR (126 MHz, CDCl₃) δ [ppm] = 131.7 (d, J = 3.4 Hz), 131.5 (d, J = 7.0 Hz), 130.8 (d, J = 9.4 Hz), 121.0 (d, J = 4.7 Hz), 62.3 (d, J = 7.0 Hz), 33.3 (d, J = 138.4 Hz), 16.5 (d, J = 6.0 Hz).

Diethyl (4-(4-(2-(5-chloro-2-methylthiophen-3-yl)cyclopent-1-en-1-yl)-5-methylthiophen-2-yl)benzyl)phosphonate (3)

Under an argon atmosphere *n*BuLi (5.0 mL, 11.4 mmol, 2.3 M in cyclohexane) was added dropwise to a solution of **1** (3.0 g, 0.46 mmol) in THF (70 mL) at 0 °C. After stirring the mixture for 1.5 h, triisopropyl borate (1.6 mL, 10.9 mmol, ρ = 0.815 g cm⁻¹) was added dropwise and stirring was continued for 1h. Meanwhile **2** (3.6 g, 11.8 mmol) was dissolved in THF (30 mL) and aqueous Na₂CO₃ (2 M, 20 mL) was added. This mixture was degassed and ethylene glycol (10 drops), as well as Pd(dppf)Cl₂*DCM (0.22 g, 0.27 mmol) were added. After stirring the mixture for 15 min at 80 °C, the solution of the boronate was added and the reaction was stirred over night at 80 °C. After cooling to room temperature, water and ethyl acetate were added. The mixture was extracted with ethyl acetate (2x). The combined organic phase was washed with brine, dried (MgSO₄) and the solvent was removed. The crude product was purified by column chromatography (ethyl acetate) and subsequently by preparative recycling-GPC to give **3** (0.97 g, 1.9 mmol) in 20% yield.

¹H-NMR (500 MHz, CDCl₃) δ [ppm] = 7.43 (d, J = 7.6 Hz, 2H), 7.26 (dd, J = 7.9, 2.8 Hz, 2H), 6.97 (s, 1H), 6.62 (s, 1H), 4.08 – 3.97 (m, 4H), 3.14 (d, J = 21.7 Hz, 2H), 2.84 – 2.72 (m, 4H), 2.08 – 2.01 (m, 2H), 1.98 (s, 3H), 1.88 (s, 3H), 1.26 (t, J = 7.1 Hz, 6H).

¹³C-NMR (126 MHz, CDCl₃) δ [ppm] = 139.6 (d, J = 2.0 Hz), 136.5 (s), 135.4 (s), 135.3 (s), 134.6 (s), 133.9 (s), 133.4 (s), 133.2 (d, J = 3.8 Hz), 130.5 (d, J = 9.4 Hz), 130.3 (d,

$J = 6.9$ Hz), 127.0 (s), 125.6 (d, $J = 3.4$ Hz), 125.1 (s), 123.9 (s), 62.3 (d, $J = 6.4$ Hz), 38.6 (s), 38.5 (s), 33.6 (d, $J = 138.0$ Hz), 23.0 (s), 16.5 (d, $J = 5.9$ Hz), 14.5 (s), 14.3 (s).

Diethyl(4-(4-(2-(5-(3,5-bis(trifluoromethyl)phenyl)-2-methylthiophen-3-yl)cyclopent-1-en-1-yl)-5-methylthiophen-2-yl)benzyl)phosphonate (5)

3,5-Bis(trifluoromethyl)phenylboronic acid (0.96 g, 3.7 mmol), Pd(OAc)₂ (0.021 g, 0.09 mmol), XPhos (0.089 g, 0.18 mmol), and K₃PO₄ (1.58 g, 7.4 mmol) were placed in a round bottom flask and were degassed. **3** (0.97 g, 1.86 mmol) was dissolved in toluene (15 mL) and the solution was added to the reaction flask. The mixture was degassed and stirred at 80 °C for 24 h. After cooling to room temperature, water and ethyl acetate were added. The organic phase was separated and washed with brine, dried (MgSO₄), and the solvent was removed. The crude product was purified by column chromatography (ethyl acetate) to give **5** (0.40 g, 0.57 mmol) in 31% yield.

¹H-NMR (500 MHz, CDCl₃) δ [ppm] = 7.85 (s, 2H), 7.69 (s, 1H), 7.43 (d, $J = 7.5$ Hz, 2H), 7.26 (dd, $J = 8.3, 2.5$ Hz, 2H), 7.15 (s, 1H), 7.00 (s, 1H), 4.08 – 3.95 (m, 4H), 3.13 (d, $J = 21.7$ Hz, 2H), 2.85 (t, $J = 7.3$ Hz, 4H), 2.14 – 2.07 (m, 2H), 2.03 (s, 3H), 2.00 (s, 3H), 1.25 (t, $J = 7.1$ Hz, 6H).

¹³C-NMR (101 MHz, CDCl₃) δ [ppm] = 139.8 (s), 137.5 (s), 137.2 (s), 136.7 (s), 136.6 (s), 136.3 (s), 135.8 (s), 134.5 (s), 134.1 (s), 133.2 (d, $J = 4.0$ Hz), 132.3 (q, $J = 33.4$ Hz), 130.6 (d, $J = 9.6$ Hz), 130.3 (d, $J = 6.6$ Hz), 126.4 (s), 125.6 (d, $J = 3.1$ Hz), 125.2 – 124.9 (m), 124.7 (s), 123.9 (s), 122.0 (s), 120.3 – 120.0 (m), 62.3 (d, $J = 6.7$ Hz), 38.6 (s), 38.6 (s), 33.6 (d, $J = 138.2$ Hz), 23.2 (s), 16.5 (d, $J = 5.8$ Hz), 14.7 (s), 14.6 (s).

(4-(4-(2-(5-(3,5-bis(trifluoromethyl)phenyl)-2-methylthiophen-3-yl)cyclopent-1-en-1-yl)-5-methylthiophen-2-yl)benzyl)phosphonic acid (PA-DAE)

A literature procedure was adapted.^[2] Phosphonic ester **5** (0.60 g, 0.86 mmol) was dissolved in dry acetonitrile (2.2 mL) and cooled to 0 °C. Trimethylsilyl bromide (0.34 mL, 2.6 mmol, $\rho = 1.16 \text{ g cm}^{-3}$) was added dropwise and the mixture was stirred over night at room temperature. Acetonitrile was removed and methanol (1 mL) was added and the mixture was stirred overnight. Upon removing the solvent, aq. KOH (approx. 1 mol L^{-1}) and CH_2Cl_2 were added to the mixture. The organic phase was extracted with aq. KOH. The combined aqueous phase was cooled to 0 °C and HCl was added until a precipitate formed. The aqueous phase was extracted with diethyl ether. The organic phase was dried and the solvent was removed to give phosphonic acid PA-DAE (0.12 g, 0.19 mmol) in 22% yield.

¹H-NMR (500 MHz, MeOD) δ [ppm] = 8.00 (s, 2H), 7.78 (s, 1H), 7.41 (s, 1H), 7.34 (s, 4H), 7.00 (s, 1H), 2.91 (d, $J = 20.3 \text{ Hz}$, 2H), 2.91 – 2.84 (m, 4H), 2.16 – 2.08 (m, 2H), 2.01 (s, 3H), 1.99 (s, 3H).

2. DFT calculations on isolated PA-DAE molecules

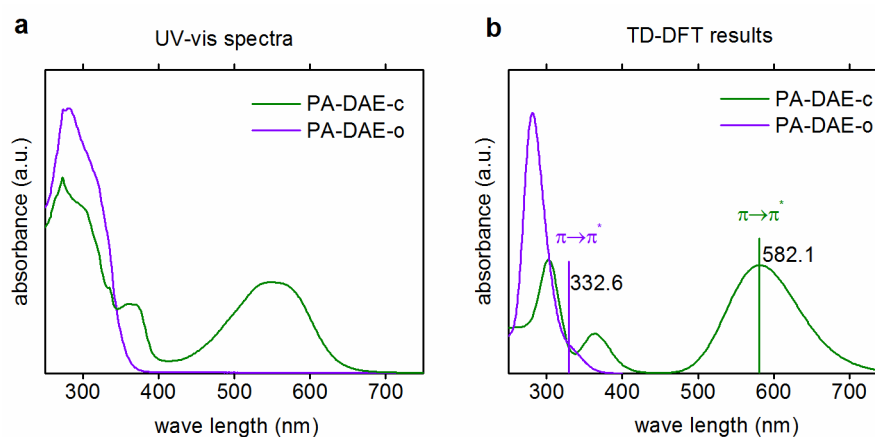


Figure S1. Comparison of absorption spectra between (a) measured UV-vis spectra and (b) TD-DFT calculations.

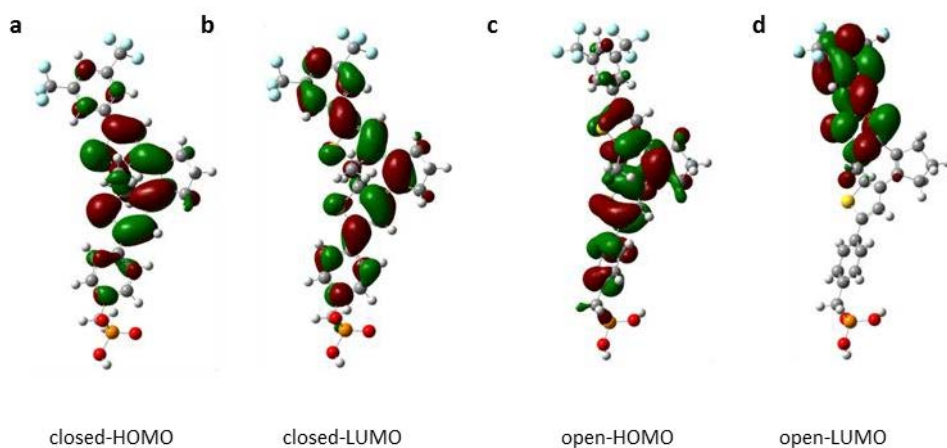


Figure S2. Calculated frontier orbitals of (a) HOMO of PA-DAE-c, (b) LUMO of PA-DAE-c, (c) HOMO of PA-DAE-o, (d) LUMO of PA-DAE-o. The isovalue is ± 0.02 a.u.

	HOMO	LUMO
closed	-4.1	-3.0
open	-4.8	-2.2

Table S1. Calculated HOMO and LUMO energy levels with the PBE functional for the isolated closed and open PA-DAE molecule. All values are in eV.

3. AFM images of the PA-DAE SAM on ZnO(000-1)

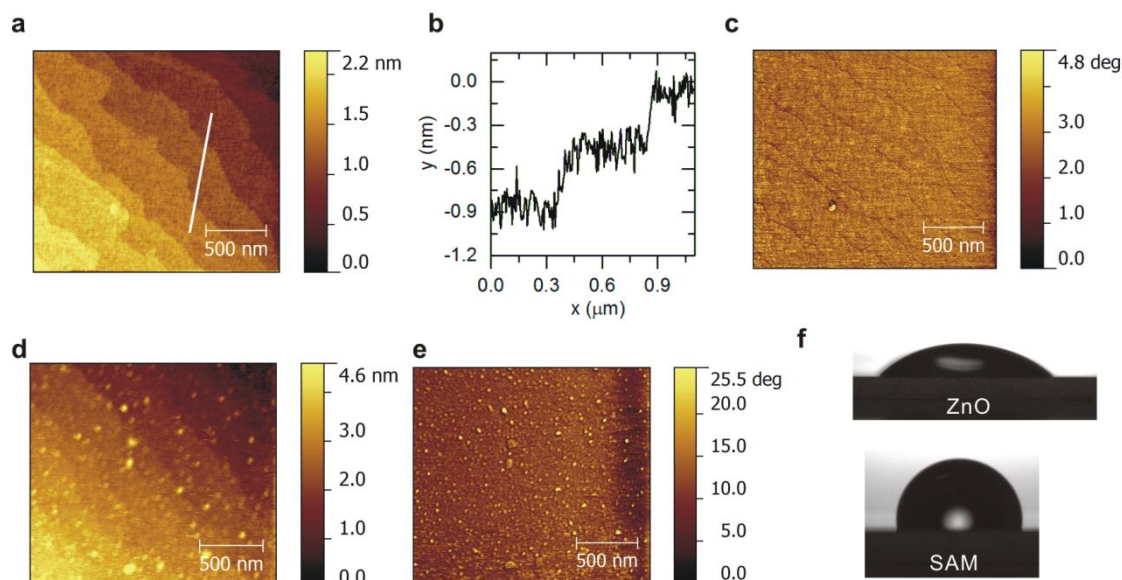


Figure S3. (a) AFM height and (c) phase images of the bare ZnO(000-1) surface. (b) Cross-section along the solid line in Figure. S3(a). (d) AFM height and (e) phase images of the PA-

DAE-o modified ZnO(000-1) surface. (f) Water contact angles of $45.5 \pm 1.0^\circ$ for bare ZnO(000-1) and $95.8 \pm 2.5^\circ$ for the SAM modified ZnO(000-1).

4. C 1s photoemission spectra

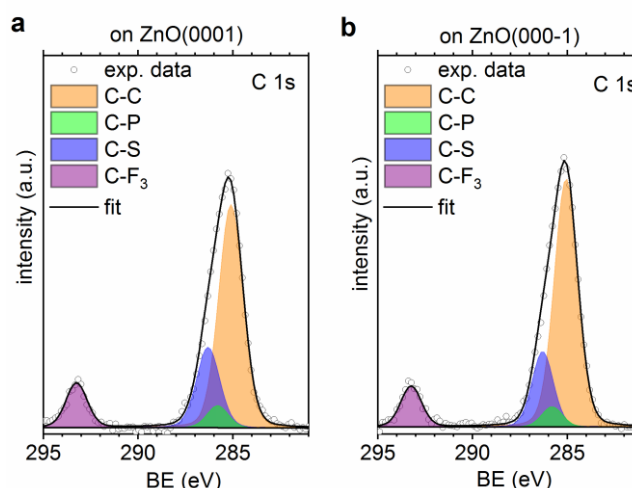


Figure S4. C 1s core electron spectra of PA-DAE-o modified (a) ZnO(0001), (b) ZnO(000-1).

Sample	C-F ₃ /C-P		C-F ₃ /C-S	
	theo	exp	theo	exp
on ZnO(0001)	2.0	2.0	0.5	0.51
on ZnO(000-1)	2.0	2.0	0.5	0.52

Table S2. C 1s peak area ratios as calculated from peak fitting of the PA-DAE modified ZnO surface in Figure S4.

The deconvolution of C1s core level spectra (Figure S4) allows us to identify different chemical species of the PA-DAE switch, i.e., carbon of the aliphatic chain (C-C/C-H) at a binding energy of 285.0 eV, carbon that binds covalently to P of the phosphonate group (C-P) at 285.8 eV, carbon that binds covalently to S (C-S) at the binding energy of 286.3 eV, and carbon of the C-F₃ tail group at 293.3 eV. The calculated peak area ratios of the carbon components are in good agreement with the theoretical ones expected for both molecules, indicating no radiation damage during the XPS data acquisition.

5. Calculating the surface coverage of the SAM

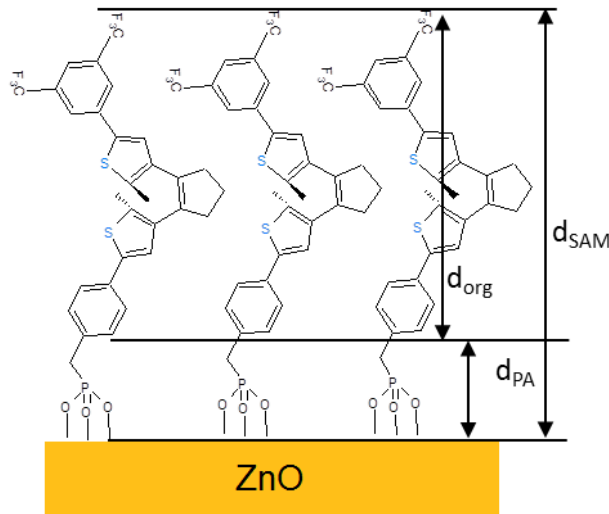


Figure S5. Schematic of the three layer model used for the calculation of PA-DAE surface density.

Considering the distribution of P and Zn atoms in the SAM, we assume that the ZnO surface is covered by the PA and the organic layer in order to obtain a homogeneous P atom distribution, and that the photoelectrons from Zn atoms are exponentially attenuated by both the PA and organic layer, while the photoelectrons from P atoms are only attenuated by the organic layer.

Originally, the intensity of the signal from the SAM is given by:^[3]

$$dI_{\text{SAM}} = I_{\text{O,SAM}} \exp(-t/\lambda_{\text{SAM}} \cos\theta) dt \quad (\text{S1})$$

$$I_{\text{SAM}} = I_{\text{O,SAM}} [1 - \exp(-d_{\text{SAM}}/\lambda_{\text{SAM}} \cos\theta)] \quad (\text{S2})$$

$$I_{\text{O,SAM}} = N I_{\text{ph}} \sigma_{\text{SAM}} \lambda_{\text{SAM}} T(E) \cos\theta \quad (\text{S3})$$

Where, d_{SAM} denotes the thickness of the SAM (see Figure S5), $I_{\text{O,SAM}}$ denotes the signal intensity of an infinitely thick film; N is the surface density of the SAM; I_{ph} is photon flux at the analysis position in photons $\text{cm}^{-2}\text{s}^{-1}$; σ_{SAM} is the photoionization cross section; λ_{SAM} is the

inelastic mean free path (IMFP); $T(E)$ is the intensity/energy response function of the spectrometer; θ is the photoelectron take-off angle, in this experiment $\theta=90^\circ$.

The intensity of the peak from the underlying ZnO is given by subtracting the attenuation of the SAM:

$$I_{\text{ZnO}} = I_{\text{O,ZnO}} \exp(-d_{\text{SAM}} / \lambda_{\text{ZnO,SAM}} \cos\theta) \quad (\text{S4})$$

where $I_{\text{O,ZnO}}$ denotes the signal intensity of an infinitely thick ZnO film; λ_{SAM} denotes the electron IMFP of the ZnO in the SAM.

Therefore, For the P 2p in Fig. 3a, the intensity of the peak can be described as:

$$I_{\text{P}} = I_{\text{O,P}} [1 - \exp(-d_{\text{PA}} / \lambda_{\text{P,PA}} \cos\theta)] \exp(-d_{\text{org}} / \lambda_{\text{P,org}} \cos\theta) \quad (\text{S5})$$

where d_{PA} is the thickness of the PA corresponding to the projection along the z axis; $\lambda_{\text{P,PA}}$ is the electron IMFP of the P 2p at the kinetic energy of ca. 100 eV in the PA layer; d_{org} is the thickness of the organic layer; $\lambda_{\text{P,org}}$ is the electron IMFP of the P 2p in the organic layer.

For Zn 3s, whose intensity is attenuated twice by both the PA and organic layer, the measured peak intensity can be described as:

$$I_{\text{Zn}} = I_{\text{O,Zn}} \exp(-d_{\text{PA}} / \lambda_{\text{Zn,PA}} \cos\theta) \exp(-d_{\text{org}} / \lambda_{\text{Zn,org}} \cos\theta) \quad (\text{S6})$$

where, $\lambda_{\text{Zn,PA}}$ is the electron IMFP of the Zn 3s at the kinetic energy of ca. 100 eV in the PA layer; $\lambda_{\text{Zn,org}}$ is the electron IMFP of the Zn 3s in the organic layer.

The attenuation of the topmost organic layer for both P 2p and Zn 3s can be cancelled by each other due to the kinetic energies of the out-coming electrons from P 2p and Zn 3s that are energetically close, thus $\lambda_{\text{P,org}} \approx \lambda_{\text{Zn,org}}$. The ratio of I_{P} to I_{Zn} is given by:

$$\begin{aligned}
\frac{I_P}{I_{Zn}} &= \frac{I_{O,P}}{I_{O,Zn}} \frac{1 - \exp(-d_{PA}/\lambda_{P,PA} \cos\theta)}{\exp(-d_{PA}/\lambda_{Zn,PA} \cos\theta)} \\
&= \frac{N_P \sigma_P \lambda_{P,PA}}{N_{Zn} \sigma_{Zn} \lambda_{Zn,ZnO}} \frac{1 - \exp(-d_{PA}/\lambda_{P,PA} \cos\theta)}{\exp(-d_{PA}/\lambda_{Zn,PA} \cos\theta)}
\end{aligned} \tag{S7}$$

where N_{Zn} is the density of the Zn atoms in ZnO (41.5 nm^{-3} in the bulk).^[7] The surface coverage of the SAMs is given by $N_P \times d_{PA}$, which is $2.2 \pm 0.6 \text{ nm}^{-2}$ for PA-DAE modified ZnO(0001), and $2.1 \pm 0.6 \text{ nm}^{-2}$ for PA-DAE modified ZnO(000-1), respectively.

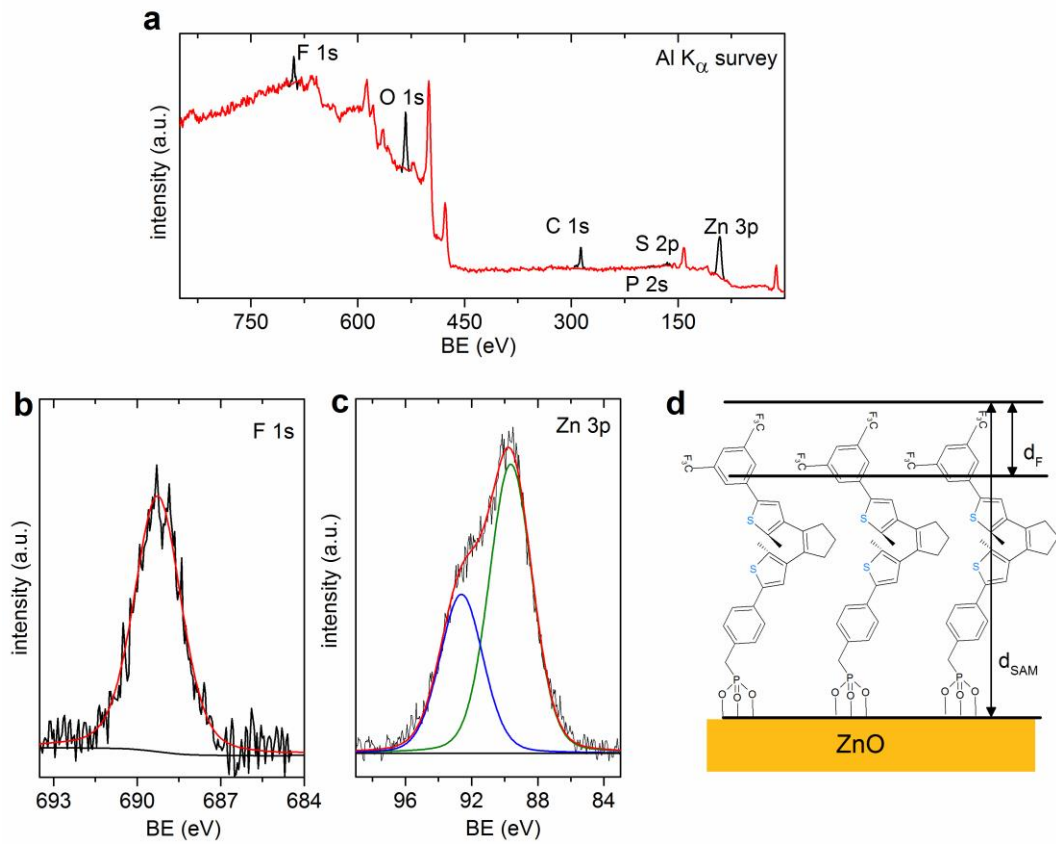


Figure S6. Al K α XPS spectra of (a) survey, (b) F 1s, (c) Zn 3p for PA-DAE-o modified ZnO(0001). (d) Three layer model for calculating the SAM density. In this model, the homogeneity of the F atoms distributed on the surface was taken into consideration.

Al K α XPS spectra were collected in a home-made set-up. Surface density of the SAMs was calculated using F 1s and Zn 3p peak area ratio:

$$\frac{I_F}{I_{Zn}} = \frac{N_F S_{F1s}}{N_{Zn} S_{Zn3p}} \frac{1 - \exp(-d_F / \lambda_F \cos \theta)}{\exp(-d_{SAM} / \lambda_{Zn,SAM} \cos \theta)} \quad (S8)$$

where S_{F1s} and S_{Zn3p} are the relative sensitivity factor (normalized to C 1s) of the F 1s and Zn 3p with values of 4.02 and 2.95, respectively, λ_F is the electron IMFP of the F 1s in the SAM, $\lambda_{Zn,SAM}$ is the electron IMFP of the Zn 3p in the SAM. The calculated surface coverage for the PA-DAE molecules is $2.3 \pm 0.7 \text{ nm}^{-2}$, close to the results obtained from equation S7.

6. Error analysis

The quantification of XPS data gives uncertainties which are determined by several factors, e.g., homogeneity of the distribution of corresponding atoms, IMFP of the photoelectrons, photoionization cross section, analyser transmission function, etc. In our calculations, according to Equation S7, we mainly consider three factors that contribute to the total uncertainty.

(1) Electron inelastic mean free path (IMFP) was calculated based on Tanuma et al. TPP-2M equation,^[4,5] which shows average root-mean-square deviations of ~17% from IMFPwin program. In the calculation the number of valence electrons per atom (for an element), molecular weight and the material band gap were taken into consideration.

(2) Partial photoionization cross section for each element was taken from Reference [6], and a normal deviation of ~10% was considered.

(3) Peak areas were calculated by the fitting of the spectra using CasaXPS. A typical standard deviation produced by the fitting is lower than 5%, as determined by Monte Carlo simulation (available within the CasaXPS software).

Based on equation S7, the error propagation is thus given by:

$$\frac{\delta N}{|N|} = \sqrt{\left(\frac{\delta \lambda}{\lambda}\right)^2 + \left(\frac{\delta \sigma}{\sigma}\right)^2 + \left(\frac{\delta f}{f}\right)^2} \quad (\text{S9})$$

where $\frac{\delta N}{|N|}$ is the total error, $\frac{\delta \lambda}{\lambda}$ is the deviation of the IMFP, that is 17%, $\frac{\delta \sigma}{\sigma}$ is the deviation of the partial photoionization cross section (10%), and $\frac{\delta f}{f}$ is the deviation produced by peak fitting. The calculated $\frac{\delta N}{|N|} \approx 30\%$, which is quite comparable to the literature value.^[7]

7. Calculating the coverage of the surface hydroxyl group

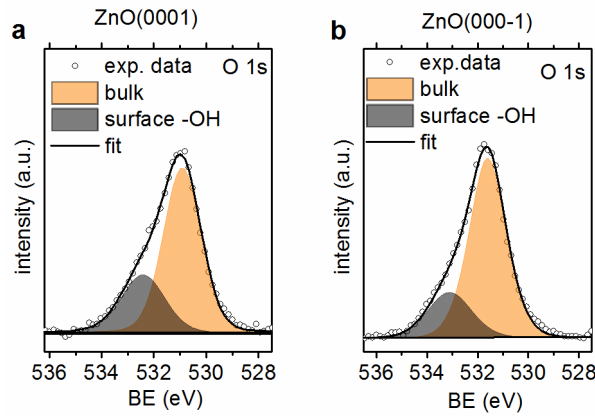


Figure S7. O 1s core level spectra of clean (a) ZnO(0001) and (b) ZnO(000-1) measured with the photon energy of 640 eV. The measured peak area ratio of surface to bulk is about 0.4.

For the clean ZnO (after sputtering), the hydroxyl groups (-OH) are commonly detected on both polar surfaces due to their stabilization mechanism. As discussed above, the surface coverage of these -OH can be estimated based on the exponential decay of the out-coming electrons:

$$\frac{I_{OH}}{I_O} = \frac{N_{OH} \times [1 - \exp(-d / \lambda_{OH})]}{N_O \times \exp(-d / \lambda_{OH})} \quad (\text{S10})$$

where I_{OH}/I_O is the peak area ratio of surface to bulk; N_{OH} is the density of the surface -OH; N_O is the density of the O atom in the bulk (41.5 nm^{-3}); d is the thickness of the surface -OH (ca. 0.25 nm); λ_{OH} is the inelastic mean free path of the out-coming electrons (0.5 nm in this

calculation). The density of -OH on both polar surfaces is calculated to be 6.0 nm^{-2} . For a fully covered surface, the density of the surface -OH is about 11 nm^{-2} calculated according to the ZnO unit cell. Therefore, the hydroxyl group on clean ZnO surfaces corresponds to a 50% surface coverage.

8. Molecular dipole components of isolated molecules

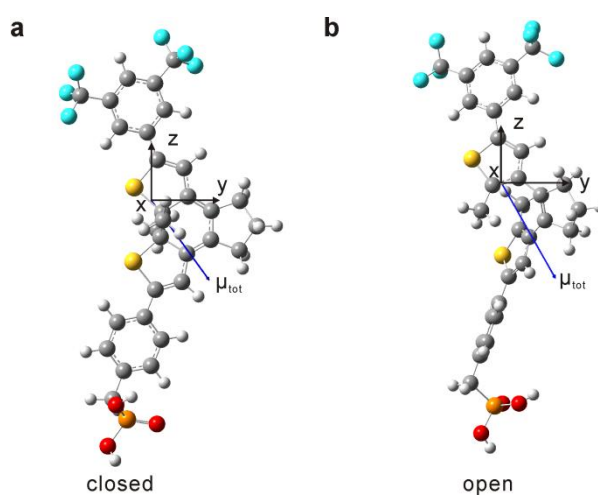


Figure S8. Molecular dipole moments for (a) closed and (b) open PA-DAE molecules, as calculated with the PBE functional and a 6-31G(d) basis set. The z axis is along the direction perpendicular to the surface

	μ_x	μ_y	μ_z	μ_{tot}
closed	0.1	2.9	-3.7	-4.7
open	2.4	1.7	-3.4	-4.5

Table S3. Dipole components of the PA-DAE molecule. All values are in Debye.

9. ZnO unit cell

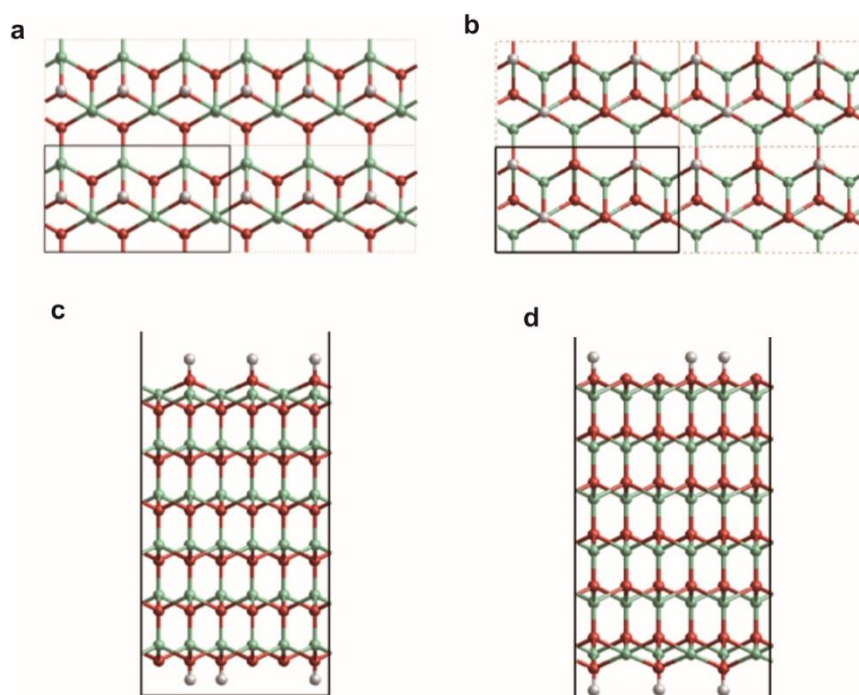


Figure S9. (a) Top and (c) side view of -OH and -H modified ZnO(0001) unit cell. (b) Top and (d) side view of -H and -OH modified ZnO(000-1) unit cell.

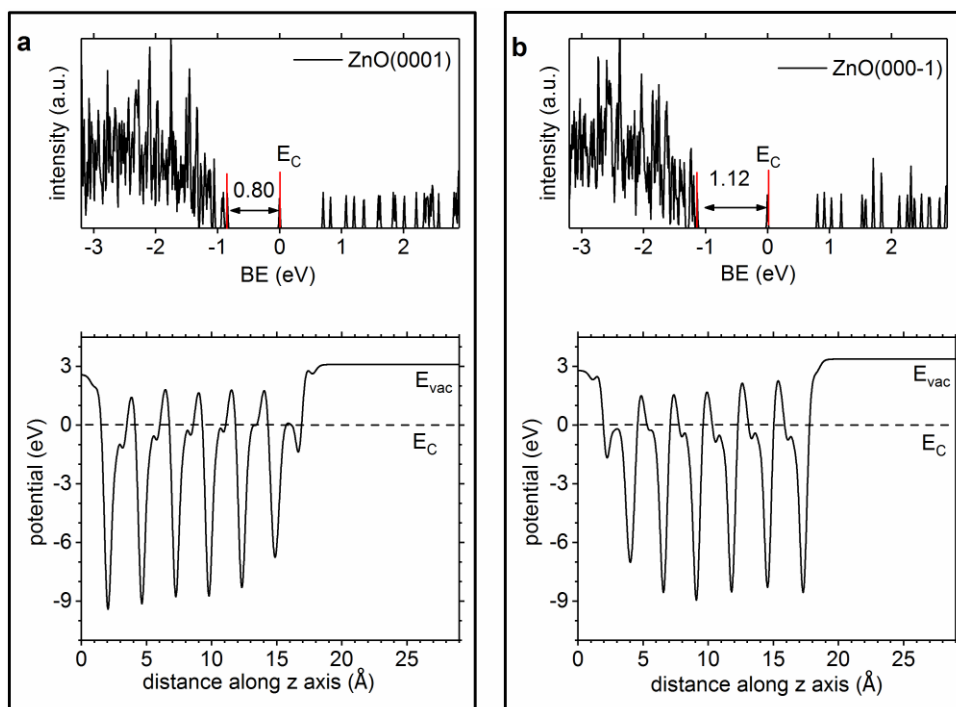


Figure S10. Total density of states (top) and plane averaged electrostatic potential (bottom) of (a) ZnO(0001) and (b) ZnO(000-1) unit cells. E_c serves as the reference of zero binding energy, the work function (ϕ_{bare}) of the slabs is given by: $\phi_{\text{bare}} = E_{\text{vac}} - E_c$.

10. Schematic illustration of the PA adsorption process

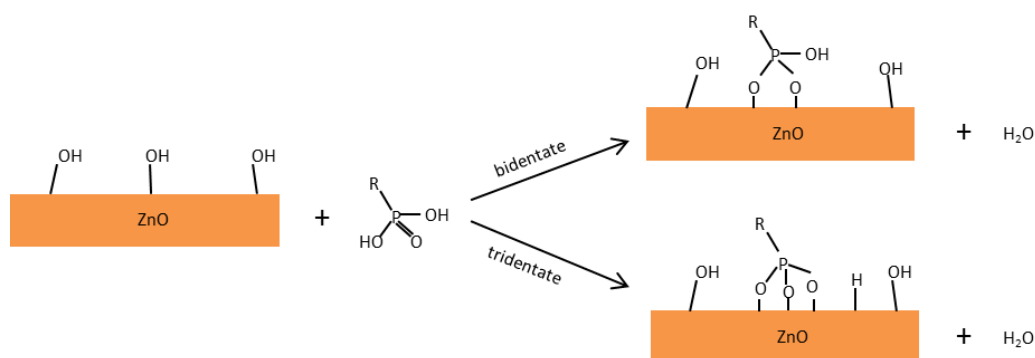


Figure S11. Schematic illustration of the surface adsorption of the PA molecule on polar ZnO surfaces. In the bidentate mode, two oxygen atoms are bonded to the ZnO surface; one hydrogen atom is lost via the formation of a water molecule, another one remains attached to PA. In the tridentate mode, three oxygen atoms are bonded to the ZnO surface. Two hydrogen atoms are removed from the PA; one reacts with the surface -OH to form a water molecule, while the other is attached to the surface.

11. Adsorption energy

The adsorption energy of the PA-DAE SAM on both polar ZnO surfaces is calculated based on the schemes illustrated in Figure S11.

For the bidentate binding:

$$\Delta E_{\text{ads}} = E_{\text{SAM}} + E_{\text{H}_2\text{O}} - (E_{\text{mol}} + E_{\text{ZnO}}) \quad (\text{S11})$$

where E_{SAM} denotes the total energy of the SAM; $E_{\text{H}_2\text{O}}$ the energy of the H_2O produced during the adsorption process; E_{mol} the energy of the neutral PA-DAE molecule; E_{ZnO} the energy

of the bare ZnO surface with the hydroxyl groups originally covered on the surface (as shown in Figure S11).

For the tridentate binding:

$$\Delta E_{\text{ads}} = E_{\text{SAM-H}} + E_{\text{H}_2\text{O}} - (E_{\text{mol}} + E_{\text{ZnO}}) \quad (\text{S12})$$

where $E_{\text{SAM-H}}$ denotes the total energy of the SAM with one hydrogen atom of PA attached to ZnO.

On ZnO(0001)	ΔE_{ads} (eV)
c-tridentate	-3.5
c-bidentate	-2.1
o-tridentate	-3.3
o-bidentate	-1.9
On ZnO(000-1)	
c-tridentate	-3.6
c-bidentate	-2.3
o-tridentate	-3.5
o-bidentate	-2.6

Table S4. Calculated adsorption energies of the SAM in tridentate and bidentate bindings on ZnO(0001) and ZnO(000-1) slabs.

12. Interface charge distribution

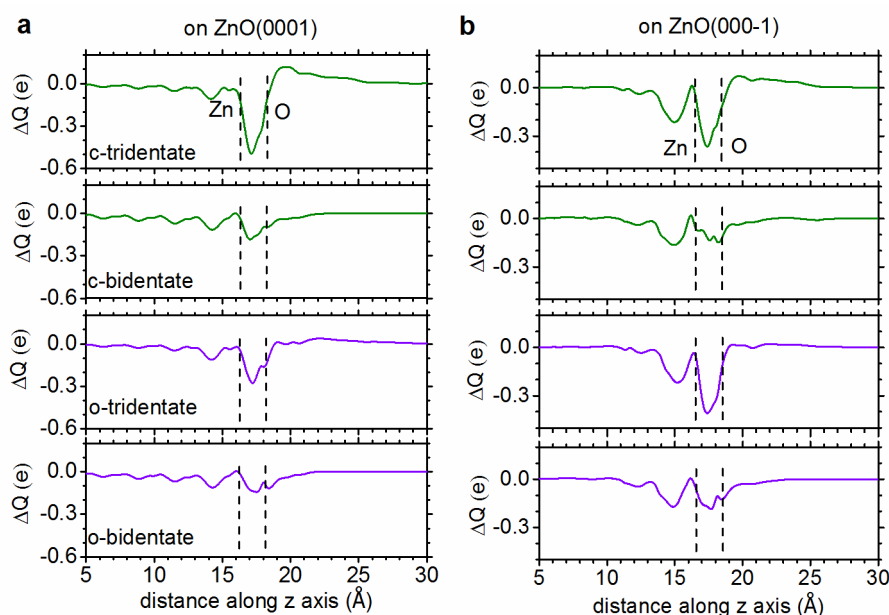


Figure S12. Cumulated charge reorganization calculated by the following equation:

$$\Delta Q(z) = \int_0^z \Delta \rho(z) dz$$

13. Bader charge analysis

On ZnO(0001)	ZnO (e)	PA-DAE (e)
c-tridentate	1.10	-1.1
c-bidentate	0.7	-0.7
o-tridentate	1.2	-1.2
o-bidentate	0.7	-0.7
On ZnO(000-1)		
c-tridentate	1.2	-1.2
c-bidentate	0.7	-0.7
o-tridentate	1.2	-1.2
o-bidentate	0.8	-0.8

Table S5. Calculated Bader charge transfer between the ZnO slab and the PA-DAE molecule.

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